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ALKALINE EARTH POLYURANATES

by

H. R. Hoekstra
J. J. Katz

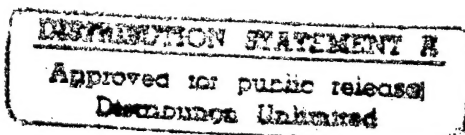
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H. R. Hoekstra and J. J. Katz

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Abstract

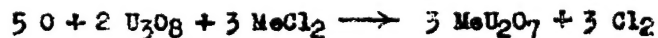
The preparation of alkaline earth polyuranates is critically discussed, and it appears that thermal decomposition of the double alkaline earth uranyl acetates provides the simplest approach to the synthesis of these compounds. MgU_2O_7 undergoes reversible decomposition at elevated temperatures. Equilibrium studies of this decomposition are described, and the phase relationships of this system are discussed. Preliminary observations on the dissociation of the calcium, strontium, and barium compounds are also discussed.

The work described here is part of a general investigation of metal uranates and polyuranates. The material given here, however, includes only the diuranates of magnesium, calcium, strontium, and barium.

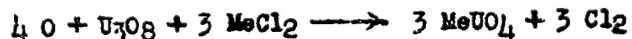
A number of methods for the preparation of these compounds may be found in the literature.

A. Dry methods.

1. Fusion of U_3O_8 or UO_3 with the alkaline earth chloride (metal oxide may also be added).



It is very difficult to completely oxidize the uranium, even on long heating. Metal chlorates may be added to hasten oxidation, but this is hazardous. Addition of the metal carbonate has been suggested to moderate the chlorate decomposition, but this further contaminates the sample with metal oxide. Method 1 has also been used as a preparative method for the uranates:



Since an excess of metal chloride is used for the ignition, it seems likely that uranate, rather than diuranate should be formed.

B. Wet methods:

2. Addition of a solution of metal hydroxide to one containing uranyl ion to precipitate the diuranate. The relative insolubility of the metal hydroxides as well as the necessity for exclusion of carbon dioxide argues against the use of this method.
3. Addition of ammonium ion to a solution containing uranyl and alkaline earth metal ions. Very dilute solutions must be used to minimize coprecipitation of ammonium diuranate which is converted to U_2O_8 on ignition.
4. Dissolution of uranyl nitrate in ether and addition of metal oxide to form the diuranate. This method has been used for the preparation of CaU_2O_7 , but it is difficult to obtain complete reaction of the oxide.
5. Precipitation of the metal-uranyl double acetate and ignition of this compound to the diuranate. This method had been described in the literature for the preparation of barium diuranate. Since the corresponding magnesium, calcium, and strontium uranyl acetates $[Me(UO_2)_2(OAc)_6 \cdot 6H_2O]$ had also been prepared, it was to be expected that ignition of these salts would give the desired products in a pure state.

The preparative method consisted in dissolving uranyl acetate and alkaline earth acetate in a minimum volume of 2 M acetic acid at about 75°C. If crystallization occurred on cooling to room temperature, the solution was then cooled to 0°C, filtered and the crystals of double acetate washed with alcohol and then with ether. If no crystallization took place on cooling to room temperature, the solution was evaporated slowly (~50°C) until it was sufficiently concentrated to crystallize on cooling.

Analyses obtained on the dried (60°C) acetates gave the results tabulated in Table 1 indicating that this method was satisfactory.

$\text{Me}(\text{UO}_2)_2(\text{OAc})_6 \cdot 6\text{H}_2\text{O}$	Double acetate analyzed			
	Mg	Ca	Sr	Ba
% alk. earth ion found	2.355	3.89		12.73
% " " " theo.	2.37	3.84		12.86* as dihydrate
% uranium found	46.35	46.0		44.25
% " " theo.	46.42	45.67		44.59*
$\frac{\text{uranium}}{\text{alk. earth}}$ ratio	2.01	1.99		2.01

Ignition of the double acetates was accomplished by heating slowly in a muffle furnace to 750°C. Decomposition appeared to be complete at ~400°C, but the samples were ignited to the higher temperature to insure completion of the decomposition. The products were identified by comparison of the change in weight on ignition with the calculated change for conversion to the diuranate. Samples were also prepared for x-ray study by Dr. Zachariasen.

Qualitative observations on the alkaline earth diuranates showed that on ignition in air they turned grey to black in color with loss in weight. Further heating at a somewhat lower temperature resulted in reconversion to the original diuranate.

Quantitative investigation of this property of magnesium diuranate, MgU_2O_7 , was carried out in the apparatus shown in Fig. 2. The results

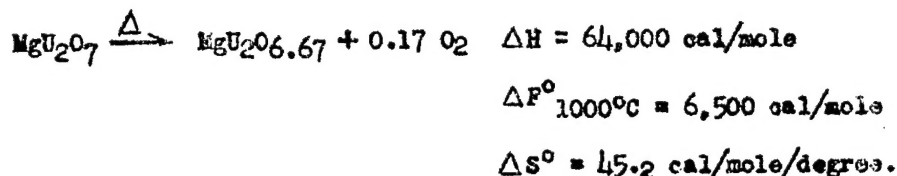
indicate that the loss of oxygen occurs in two steps, the formula of the first decomposition product being $\text{MgU}_2\text{O}_{6.67}$, and of the second MgU_2O_6 . The formulas were determined by measuring the volume of oxygen required to reconvert to MgU_2O_7 . Equilibrium pressures of oxygen over MgU_2O_7 - $\text{MgU}_2\text{O}_{6.67}$ and $\text{MgU}_2\text{O}_{6.67}$ - MgU_2O_6 mixtures have been obtained and are given in Table 2. The pressures are reproducible and do not depend on the way in which equilibrium is approached.

Table 2

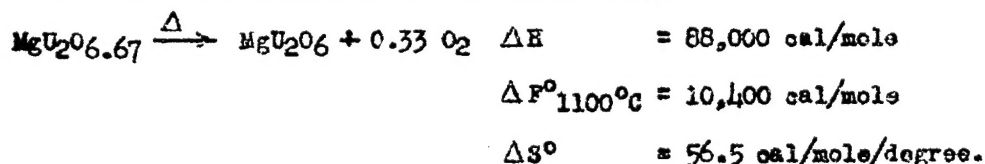
Equilibrium Oxygen Pressures over MgU_2O_7 - $\text{MgU}_2\text{O}_{6.67}$
and $\text{MgU}_2\text{O}_{6.67}$ - MgU_2O_6 Mixtures

Temp. (°C)	Equilibrium Oxygen Pressure (mm)	
	MgU_2O_7 - $\text{MgU}_2\text{O}_{6.67}$	$\text{MgU}_2\text{O}_{6.67}$ - MgU_2O_6
800	0.5	-
850	2.0	-
900	7.5	-
950	19.0	-
1000	55.0	1.0
1025	93.0	2.5
1050	148	5
1075	-	9
1100	-	16.5
1125	-	32.0

The respective heats of reaction can be calculated from the equilibrium pressures. For the first reaction:



The estimated temperature at which the equilibrium pressure would be 1 atmosphere is 1145°C , and the approximate temperature at which MgU_2O_7 will decompose in air is 1055°C . Since the pressures obtained are equilibrium pressures, according to the phase rule there must be two solid phases present--i.e., the mixture cannot be a solid solution of continuously varying composition. The same holds true for the second step:



The temperature at which the oxygen pressure reaches one atmosphere is 1300°C for this reaction, and air equilibrium is attained at about 1200°C .

The oxidation of MgU_2O_6 and $\text{MgU}_2\text{O}_{6.67}$ has been studied to determine semi-quantitatively the rate of reaction and the heat of activation, and, if possible, to find out something concerning the mechanism of the reaction. The following observations were made.

1. The rate of oxidation is independent of oxygen pressure, except possibly at extremely low pressures.
2. The oxidation of $\text{MgU}_2\text{O}_{6.67}$ takes place at the rate of 2.4 per cent/min at 730°C , and 1.2 per cent/min at 700°C . These values give an approximate heat of activation of 36,000 cal/mole.
3. The oxidation of MgU_2O_6 takes place at a lower temperature, the rate at 550°C being comparable with that of $\text{MgU}_2\text{O}_{6.67}$ at 700°C . At 550°C , the calculated oxidation rate of $\text{MgU}_2\text{O}_{6.67}$ is 0.04 per cent/min. It has not been determined whether the oxidation of MgU_2O_6 takes place in one or

more steps. A plot of log per cent MgU_2O_6 vs time does not give a straight line, but it is difficult to picture a two-step reaction when it has been shown that $\text{MgU}_2\text{O}_{6.67}$ does not react at this temperature.

4. As the reaction tube containing either MgU_2O_6 or $\text{MgU}_2\text{O}_{6.67}$ is initially heated to the reaction temperature of 500° or 700°C for each run, in the first minute a preliminary absorption of oxygen is observed amounting to about 13 per cent of the calculated amount required for complete oxidation. Further investigation of this portion of the oxidation process indicated that it was not a surface phenomenon since grinding of the sample to increase surface area did not alter the percentage of oxygen reacting. X-ray samples taken at both extremes of the 13% range showed only one phase in each case.

Oxygen absorption occurred at temperatures as low as 200°C (compared with $\sim 500^\circ\text{C}$ for the remainder of the reaction). These observations indicate that there may be a range of solid solution between $\text{MgU}_2\text{O}_{5.94}$ and $\text{MgU}_2\text{O}_{6.08}$.

Dr. Zachariassen has indicated that the compound MgU_2O_7 may actually not be a single phase but rather a mixture of MgUO_4 and a second phase which may be $\text{MgU}_3\text{O}_{10}$.

Preliminary observations indicate that the other alkaline earth diuranates also lose oxygen at elevated temperatures, and similar studies are in progress.